# Behaviour of metamitron and hydroxy-chlorothalonil in low-humic sandy soils

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**Abstract: The behaviour of the herbicide metamitron and of the main transformation product, hydroxy-chlorothalonil (HTI), of the fungicide chlorothalonil was studied to assess the risk of leaching from low-humic sandy soil. The adsorption of metamitron corresponded to a $K_{om}$ value of about 60 dm$^3$ kg$^{-1}$ (moderate adsorption). The half-life of metamitron in soil at 15 °C was only three days, presumably due to adaptation of the micro-organisms. In the autumn, the residue of metamitron in the soil profiles corresponded to less than 1% of the cumulative dosage. The half-life of chlorothalonil at 15 °C was about 12 days and about 45% of it was transformed to HTI. The adsorption of HTI to the soils corresponded to a $K_{om}$ value of 260 dm$^3$ kg$^{-1}$. The incubation study (15 °C) showed the transformation of HTI in the soils to be very slow. The amounts of HTI remaining in the soil profiles in the autumn corresponded to 4 and 16% of the cumulative dosage of chlorothalonil. In winter, the HTI residue decreased by 40% relative to the autumn level. Occasionally, HTI could be detected in the upper ground-water level (at a depth of about 1 m), at an average concentration of 0.1 to 0.2 μg dm$^{-3}$.**


**Keywords:** herbicide; pesticide; chlorothalonil; adsorption; transformation; leaching; ground-water; chemical analysis

## 1 INTRODUCTION

Growing flower bulbs is the main activity at 3300 farms in the Netherlands. Unfortunately, bulb crops are threatened by various insect pests, fungal diseases and weeds. The quality requirements with respect to plant health are very strict in the trade channels for flower bulbs. Attempts are being made to introduce methods of integrated pest management, but this takes much time. In the meantime, the use of pesticides is still rather extensive compared to their use for most other crops.

The low-humic sandy soils in the coastal region of the Netherlands are used intensively for growing flower bulbs. These soils are considered to be vulnerable to the leaching of pesticides to the ground-water, which is at shallow depths. These regions are also used as ground-water catchment areas for public water supply. Furthermore, pesticide residues are regularly detected in the monitoring programs of the Water Boards for the water courses in flower-bulb growing areas. One of the possible pathways of contamination of the water courses is pesticide leaching through the soil.

More information was therefore needed on the contribution of leaching through low-humic sandy soils to pesticide contamination of ground-water and water courses. Two model compounds, the herbicide metamitron and hydroxy-chlorothalonil (HTI), an important transformation product of the fungicide chlorothalonil, were selected in this study.

Measurements on the adsorption of metamitron to 18 loamy soils[1] have allowed calculation of the average value of $K_{om}$, the adsorption coefficient based on soil organic matter. This value was calculated to be 108 dm$^3$ kg$^{-1}$ ($n = 18$; $s = 18$ dm$^3$ kg$^{-1}$), which points to only moderate adsorption, especially to soils low in organic matter content. When metamitron was incubated in the 18 soils at 20 °C,[1] the average value of the first-order rate coefficient of its transformation was found to be 0.027 day$^{-1}$ ($n = 18$; $s = 0.012$ day$^{-1}$). This corresponds to an average half-life of 26 days. In the Dutch pesticide regulation procedure, the properties of metamitron were considered to present the risk of some leaching from low-humic soils to shallow ground-water.

The adsorption of chlorothalonil to three soils has been measured by batch equilibration.[2] From these results, the average value of the adsorption coefficient based on organic matter, $K_{om}$, was calculated to be 1030 dm$^3$ kg$^{-1}$, indicating strong adsorption. The extent of transformation of chlorothalonil in a moist silty loam soil after seven days of incubation has also been measured.[3] Translated to 20 °C, the 50% transformation times were calculated to be in the range of five to 12 days. Another study[4] determined the rate of transformation of chlorothalonil in three

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| Field | Wassenaar M | Wassenaar C | St Maartensbrug |
|---|---|---|---|
| Clay (0–2 μm;%) | 2.3 | 2.0 | 2.9 |
| Silt (2–50 μm;%) | 1.6 | 0.9 | 2.1 |
| Organic matter (%) | 1.0 | 1.2 | 1.7 |
| $CaCO_3$ (%) | 1.3 | 1.4 | 0.1 |
| pH-KCl | 7.3 | 7.4 | 6.6 |

**Table 1.** Composition and pH of the soils in the top 0.25 m of the experimental fields

moist soils at 30 °C. Translated to 20 °C, the half-lives were calculated to be 7, 25 and 47 days, respectively. Based on these data, the risk of leaching of chlorothalonil itself to ground-water is considered to be very low.

Hydroxy-chlorothalonil (4-hydroxy-2,5,6-trichloro-isophthalonitrile; HTI) is the main transformation product of chlorothalonil in soils.[5] HTI was expected to be more mobile in soil than the parent compound and to be more persistent. However, there was much uncertainty on the extent of adsorption of HTI and on its rate of transformation in soils. Hence the basis for estimating the leaching of HTI to ground-water was very weak.

In the present study, field experiments were carried out at two flower-bulb farms with low-humic sandy soils, where metamitron and chlorothalonil were being used in practical schemes of crop protection. One farm was in Wassenaar (Province of South-Holland) and the other was in St Maartensbrug (Province of North-Holland), 75 km north of Wassenaar. Concentration profiles of metamitron and HTI in the soil were measured at the end of the growing season and during the following spring. Adsorption isotherms and transformation rates for the pesticide–soil combinations were determined in the laboratory.

## 2 PROCEDURES

### 2.1 Adsorption to the soils

#### *2.1.1 Metamitron*

About 20 sub-samples were taken from the 0.25-m top layer of the Wassenaar M and St Maartensbrug fields used to study the behaviour of metamitron. The soils were sieved (4 mm) and thoroughly mixed. Characteristics of the soils are given in Table 1. The adsorption of metamitron was measured in a batch equilibration experiment. A 50-g portion of moist soil (with known moisture content) was weighed into a glass centrifuge tube (90 $cm^3$) and equilibrated with 50 $cm^3$ metamitron solution in water (0.01 mole $CaCl_2\,dm^{-3}$). The experiment was carried out in triplicate for each of three initial concentrations of metamitron in the range of 0.1 to 1.0 $\mu g\,cm^{-3}$. The tubes were closed with ground-glass stoppers and slowly rotated (18 rev $min^{-1}$) for a day on a disc at an angle of 1.4 rad placed at 15 °C. After equilibration, the tubes were centrifuged (thermostat at 15 °C) at 2400 rev $min^{-1}$ for 20 min and a subsample of the water layer was taken for analysis by HPLC.

#### *2.1.2 HTI*

Soil samples were taken from the top layer of the Wassenaar C and St Maartensbrug fields (Table 1) used to study the behaviour of HTI. The adsorption of HTI was measured using a combination of 5 g moist soil and 5 $cm^3$ aqueous solution in 11-$cm^3$ centrifuge tubes. The three concentrations of HTI in the added solutions were in the range of 0.2 to 2.3 $\mu g\,cm^{-3}$. In other respects, the procedure was the same as that for metamitron. The equilibrium solutions in the water layer (after centrifugation) were used directly for chemical analysis by HPLC.

### 2.2 Incubation in the soils

#### *2.2.1 Metamitron*

The rate of transformation of metamitron in topsoil material from the Wassenaar M and St Maartensbrug experimental fields (Table 1) was measured in an incubation study, which started at three weeks after collection of the soils. A 100-g portion of moist soil was weighed into each of the incubation flasks (250 $cm^3$). The contents of metamitron in the soils taken from the field were found to be 0.002 $\mu g\,g^{-1}$ (Wassenaar M) and 0.026 $\mu g\,g^{-1}$ (St Maartensbrug). Using a syringe, 4 $cm^3$ of aqueous metamitron solution (26 $\mu g\,cm^{-3}$) was dosed onto the surface of the soil in each of the flasks, after which soil and solution were mixed. The flasks were covered with aluminium foil with a small hole, placed in a box with a water layer (to prevent drying out) and incubated at 15 °C in a constant-temperature cabinet. The dose of metamitron was checked to be 101 μg ($n = 20$, $s = 2$ μg) per flask; the initial content of metamitron was 0.98 $\mu g\,g^{-1}$ (on moist soil basis). The soil moisture contents during incubation were 0.13 $g\,g^{-1}$ (Wassenaar M soil) and 0.16 $g\,g^{-1}$ (St Maartensbrug soil).

At several times during the 96-day period of incubation, 50 g of soil from each flask was extracted by shaking for 1 h with acetone + water (2 + 1 by volume; 50 $cm^3$). The liquid layer was separated by centrifugation and a sub-sample of 40 $cm^3$ was taken to remove the acetone in a rotavapor at 40 °C. The remaining water layer was extracted with dichloromethane (25 $cm^3$). After evaporation of this solvent, the residue was taken up in the HPLC mobile phase, methanol + water (1 + 1 by volume). The recovery of metamitron extraction from the two soils was measured to be 87% ($n = 14$; $s = 5\%$).

#### *2.2.2 Chlorothalonil*

The soils used for the chlorothalonil incubation study were collected from the top layer of the Wassenaar C

**Table 2.** Application dates and rates of metamitron and chlorothalonil for the experimental fields near Wassenaar and St Maartensbrug in 1993. Dosages of active ingredient

| *Field, crop and compound* | *Date* | *Rate (kg ha$^{-1}$)* | *Field, crop and compound* | *Date* | *Rate (kg ha$^{-1}$)* |
|---|---|---|---|---|---|
| Wassenaar M, Lilies, | 21 April | 0.70 | St Maartensbrug, Lilies, | 20 April | 2.1 |
| Metamitron | 11 May | 0.53 | Metamitron | 19 May | 2.1 |
| | 24 May | 0.53 | | 22 July | 2.1 |
| | 4 June | 0.35 | | | |
| | 12 June | 0.35 | St Maartensbrug, Lilies | 20 April | 0.75 |
| | 28 June | 0.35 | Chlorothalonil | 30 April | 0.75 |
| | 12 July | 0.35 | | 10 May | 0.75 |
| | 21 July | 0.35 | | 19 May | 0.75 |
| | 4 August | 0.35 | | 1 June | 0.75 |
| | 11 August | 0.35 | | 20 June | 0.75 |
| | 21 August | 0.35 | | 8 July | 0.75 |
| | 8 September | 0.70 | | 6 August | 0.75 |
| | | | | 18 August | 0.75 |
| Wassenaar C, Hyacinths, | 21 April | 0.75 | | 31 August | 0.75 |
| Chlorothalonil | 1 May | 0.75 | | 11 September | 0.75 |
| | 21 May | 0.75 | | 20 September | 0.75 |

and St Maartensbrug fields (Table 1) at four weeks before the start of the incubation study. As the solubility of chlorothalonil in water is low, a dilution of formulated product (500 g litre$^{-1}$ SC) was dosed onto the soils. A volume of 4 cm$^3$ of diluted suspension (well-mixed) was applied to 100 g of soil in each of the flasks and then thorougly mixed in. The initial contents of chlorothalonil in the soils were 13.3 μg g$^{-1}$ (Wassenaar C) and 12.5 μg g$^{-1}$ (St Maartensbrug), respectively (on a moist soil basis).

At nine intervals over a period of four months, chlorothalonil was extracted from 25-g soil samples by shaking for 1 h with 7.5 cm$^3$ water and 25 cm$^3$ dichloromethane. The organic layer was isolated and evaporated, and the residue was taken up in 5 cm$^3$ hexane. The efficiency of the extraction of chlorothalonil was found to be 84% ($n = 17$; $s = 11\%$). The contents of chlorothalonil in the soils collected from the field were less than 0.005 μg g$^{-1}$. HTI was extracted by shaking 25 g soil with acetone + water (1 + 1 by volume; 50 cm$^3$) for 1 h. A volume of 40 cm$^3$ of the liquid layer was transferred to a rotavapor and the acetone was evaporated at 40 °C. The pH of the aqueous solution was lowered by adding hydrochloric acid (37%; 2.5 cm$^3$) and HTI was then extracted with 25 cm$^3$ dichloromethane. The solvent layer was isolated and evaporated; the residue was redissolved in HPLC water. The efficiency of the extraction and analysis of HTI was measured to be 103% ($n = 9$; $s = 6\%$). The contents of HTI in the soils collected from the field were 0.024 μg g$^{-1}$ (Wassenaar C) and 0.055 μg g$^{-1}$ (St Maartensbrug).

## 2.3 Field experiments

### *2.3.1 Wassenaar*

At the Wassenaar M experimental field, metamitron was applied to a crop of lilies. The size of the sampling plot in this field was 40 × 70 m. Due to occasional ploughing of the soil to a depth of 0.5 m, the composition of the 0.25 to 0.50-m layer was the same as that of the top layer (Table 1). In the sandy subsoil, the organic matter content decreased to 0.5% in the 0.75 to 1.0 m layer. The lily bulbs were planted on 30 March 1993. Soil cover by the crop gradually increased to 20% in mid-May and to about 40% in the summer months. In the course of spring and summer, the plot was sprayed 12 times with a low rate of metamitron, according to current practice at the farm. The dates of application (by a tractor-mounted field sprayer) and the dosages are given in Table 2. The lilies were harvested on 2 December 1993. During this harvest, the soil was rooted up (to a depth of 0.25 m) and this was followed soon by rotary digging (to a depth of 0.25 m) and planting of tulip bulbs (at a depth of 0.15 m).

The second experimental field, Wassenaar C, at the farm near Wassenaar, was grown with hyacinths, which were sprayed with chlorothalonil. The size of the sampling plot was 40 × 56 m. In the sandy subsoil below the cultivated top layer (occasionally to a depth of 0.5 m), the organic matter content decreased to 0.5% in the 0.75 to 1.0 m layer. The bulbs were planted on 23 September 1992. Soil cover by the crop increased to 35% at the end of April 1993 and to a maximum of 80% at the end of May. This field was sprayed with chlorothalonil at three times during the period April to May 1993 (see Table 2). The hyacinth bulbs were harvested on 16 June 1993. At this harvest, the soil was rooted up (to a depth of 0.25 m) and soon after that, the soil was rotary harrowed (to a depth of 0.15 m). There were no further cultivations up to the end of the experiment in April 1994.

The Wassenaar fields containing the sampling plots were tile-drained at a depth of 0.8 m; the distance between the tile drains was 40 m. Fertilizers were applied according to current practice.

The soil of the Wassenaar M field (down to a depth of 0.8 m) was sampled for the first time on 29 March 1993, to measure the concentrations of metamitron in the profile before the 1993 series of applications started. During the 1992 growing season, there had been 11 applications of metamitron (the last one on 31 August). The cumulative dosage in 1992 was 5.2 kg ha$^{-1}$.

After the applications during the 1993 growing season, the soil profile of the Wassenaar M and C plots was sampled twice on 8 November 1993 and on 30 March 1994. First, a stainless-steel cylindrical auger was pressed and hammered down to a depth of 0.4 m and the soil core was divided into the 0 to 0.2-m and 0.2- to 0.4-m layers. Subsequently, the auger was driven down to a depth of 0.8 m and the cores from the 0.4- to 0.6-m and 0.6- to 0.8-m layers were collected separately. Care was taken to prevent any contamination of the soil from one layer with soil from another layer. Each time, four soil cores were taken in each of the quadrants of the experimental plot (total of 16 cores per plot). The soil samples from each soil layer in a quadrant were combined and mixed before extraction, so there were four analyses for each layer in a plot. At most sampling sessions, the paths between the beds were sampled in the same way.

Cumulative rainfall in Wassenaar between the first pesticide application in the spring of 1993 and the soil sampling in the autumn was 572 mm. Between the autumn 1993 and spring 1994 samplings, cumulative rainfall was 367 mm. Soil temperature at 0.2 m depth in soil ranges from around freezing point in mid-winter to around 20 °C in mid-summer.

*2.3.2 St Maartensbrug*

At the farm near St Maartensbrug, metamitron and chlorothalonil were applied to the same experimental field grown with lilies. The size of the sampling plot was 32 × 160 m. Due to occasional ploughing to a depth of 0.5 m, the soil composition in this layer was the same as that given in Table 1. In the sandy subsoil, the organic matter content decreased to 0.9% in the 0.75- to 1.0-m layer. The lily bulbs were planted on 24 March 1993. In the spring, soil cover by the lily crop gradually increased to its maximum of 40% from June to August; from September on it was 30%. The dates of application and the dosages are given in Table 2. The chemicals were applied with a tractor-mounted field sprayer, according to normal practice. The lily bulbs were harvested on 2 November 1993. The soil was then rooted up (0.15 m deep), soon followed by ploughing (0.35 m deep) and the planting of tulip bulbs (0.15 m deep). There were no further cultivations up to the end of the experiment in the spring of 1994.

The field at St Maartensbrug was tile-drained at a depth of 0.8 m; the distance between the tile-drains was 5 m. Fertilizers were applied according to practice.

In St Maartensbrug, the field was sampled for the first time on 20 April 1993, before the 1993 applications started. The last application of metamitron, at a rate of 1.0 kg ha$^{-1}$, was in August 1992.

The soil profile of the St Maartensbrug plot was sampled at two intervals after the applications in the growing season of 1993: on 25 October 1993 and on 6 April 1994. The sampling procedure was the same as that used in Wassenaar.

At seven times during the period of April to July, the plot was sprinkler irrigated. Cumulative rainfall plus sprinkler irrigation in St Maartensbrug between the first pesticide application in spring 1993 and the soil sampling in the autumn was 821 mm. Between the autumn 1993 and spring 1994 samplings, cumulative rainfall was 417 mm.

*2.3.3 General*

At various times during the growing season, shortly after the application of a chemical, its quantity in the top layer of the soil was measured. Soil cores (diam. 4 cm) were taken down to a depth of 5 cm, at 40 locations in the plot. The soil was mixed and subsample was extracted for chemical analysis.

The ground-water in the experimental fields was first sampled in early spring 1993, before the chemicals were applied. Subsequently, groundwater was sampled five times in the period from the summer of 1993 to the spring of 1994. A casing tube with a steel cutting ring at the bottom end was pressed stepwise into the soil, while coring and bailing the soil material from inside the tube. When the required depth of 1.2 m had been reached, the ground-water sampling tube was placed, with its filter part at a depth between 0.8 and 1.2 m. The casing tube was then pulled up, while the space around the ground-water tube was filled in with the original sandy soil material. Six ground-water tubes were installed in each experimental field. Before sampling the ground-water, the first 10 dm$^3$ of water were discarded (Wassenaar) or the ground-water tube was emptied three times at intervals (St Maartensbrug). The ground-water samples were collected via a narrow stainless-steel tube into a glass flask (1 dm$^3$) by applying suction with a small battery-powered pump.

## 2.4 Extraction of the field samples

*2.4.1 Metamitron*

Metamitron was extracted from 100 g moist soil by shaking it with 25 cm$^3$ water and 50 cm$^3$ acetone for 1 h. A fraction of the liquid layer (50 cm$^3$) was placed on a water bath (40 °C) and the acetone was evaporated with the aid of a flow of nitrogen gas. The aqueous solution was extracted with dichloromethane (30 cm$^3$), after which the solvent was evaporated. The residue was taken up in HPLC mobile phase (methanol + water; 2 + 3 by volume; 2.5 cm$^3$) for analysis. The recovery of metamitron extraction from the soils, measured at six times during the study, was 69% ($n$ = 18; $s$ = 15%). The measurements were corrected for this recovery percentage.

Metamitron in a volume of 250 cm$^3$ ground-water

was extracted three times with 50 $cm^3$ dichloromethane. The solvent was removed in a rotary evaporator on a water bath (40 °C). The residue was taken up in methanol + water (2 + 3 by volume; 2.5 $cm^3$) for HPLC analysis. The recovery of the extraction was 68% ($n = 6$; $s = 6\%$); the measurements were corrected for this recovery.

*2.4.2 Chlorothalonil*

For the extraction of chlorothalonil, a subsample of 50 g moist soil was put in a flask (250 $cm^3$), 15 $cm^3$ water plus 50 $cm^3$ dichloromethane were added and the contents of the flask were shaken for 1 h. The dichloromethane layer was collected, after which the solvent was evaporated by means of a flow of nitrogen gas on a water bath at 40 °C. The residue was taken up in 5 $cm^3$ hexane and the concentrations were measured by HPLC. The average recovery of chlorothalonil from the soils was 117% ($n = 4$; $s = 6\%$)

*2.4.3 HTI*

HTI was extracted from 100 g moist soil by adding 25 $cm^3$ water an 50 $cm^3$) acetone, followed by shaking for 1 h. A fraction of the acetone-water layer (50 $cm^3$) was placed in a water bath (40 °C) and the acetone was evaporated with the aid of a flow of nitrogen gas. The aqueous solution was acidified with hydrochloric acid (37%; 5 $cm^3$) and then extracted with 30 $cm^3$ dichloromethane. This solvent was evaporated and the residue was taken up in HPLC water. The average recovery of HTI extraction from the soil samples taken in the field experiment was 71% ($n = 7$; $s = 18\%$). The measurements were corrected for this recovery percentage.

For the extraction of HTI from ground-water (250 $cm^3$), the latter was first acidified with hydrochloric acid (37%; 5 $cm^3$) and then shaken with dichloromethane (50 $cm^3$). The extract was placed in a water bath (40 °C) and the solvent was evaporated with the aid of a flow of nitrogen gas. The residue was taken up in HPLC water (2.5 $cm^3$) for analysis. The recovery of the extraction was 69% ($n = 9$; $s = 13\%$); the measurements were corrected for this recovery.

## 2.5 Chemical analysis

*2.5.1 Metamitron*

Metamitron was analysed by liquid chromatography (HPLC). The autosampler (ISS-100; Perkin-Elmer) injected 20 $mm^3$ of herbicide solution into the mobile phase. The stainless-steel column (length 125 mm; ID 4 mm) contained Lichrospher 100 RP18 (particle size 5 μm; Merck) and was mounted in an oven at 40 °C. The mobile phase of methanol + water (2 + 3 by volume) was pumped (Waters model 510) through the column at a flow rate of 1.0 $cm^3 min^{-1}$. Metamitron was detected with a UV detector (LC 90 UV; Perkin-Elmer) at a wavelength of 310 nm. The detector signal was processed with the Multichrom data system (VG Data Systems). The concentrations were calculated using the calibration line obtained by injecting standard solutions with concentrations in the range of 0.01 to 3.0 $\mu g\,cm^{-3}$.

*2.5.2 Chlorothalonil*

Chlorothalonil was analysed by HPLC, using a glass separation column (length 10 cm) filled with Chrom-Spher Si (Chrompack). The mobile phase of hexane + dioxane (99 + 1 by volume) was pumped through the column at a flow rate of 1.0 $cm^3 min^{-1}$. Chlorothalonil was detected with a diode-array detector (LC-235; Perkin-Elmer) at a wavelength of 255 nm. The concentrations in the standard solutions injected for the construction of the calibration line were in the range of 0.05 to 10.0 $\mu g\,cm^{-3}$.

*2.5.3 HTI*

In the analysis of HTI by HPLC, the separation column (length 20 cm; ID 3 mm) contained Chrom-Spher C18 (Chrompack). The mobile phase was sodium acetate buffer in water (pH 5.3) plus methanol (1 + 1 by volume) and was pumped through the column at a flow rate of 0.5 $cm^3\ min^{-1}$. HTI was detected by the UV detector (LC 90 UV, Perkin-Elmer) at a wavelength of 245 nm. Standard solutions with concentrations in the range of 0.01 to 1.0 $\mu g\,cm^{-3}$ were injected for the construction of the calibration line.

HTI in six ground-water samples was also analysed by TNO Nutrition and Food Research in Zeist, the Netherlands, who first methylated HTI with diazomethane and then measured the reaction product by gas-liquid chromatography. Details of this method are given by Van Doorn *et al*.[6]

## 2.6 Calculations

The adsorption of the compounds to the soils was described with the following form of the Freundlich equation:

$$X = K_f c_r (c_l / c_r)^n$$

with: $X$ = amount adsorbed, mg $kg^{-1}$;

$K_f$ = Freundlich adsorption coefficient, $dm^3\,kg^{-1}$;
$c_l$ = concentration in solution, $mg\,dm^{-3}$;
$c_r$ = reference concentration, $mg\,dm^{-3}$;
$n$ = Freundlich exponent, -.

The advantage of this equation is that the unit of $K_f$ is independent of the exponent $n$. The value of $c_r$ was selected to be 1 $mg\,dm^{-3}$.

The transformation of metamitron and chlorothalonil in soil was described by first-order kinetics. For HTI, both its formation from chlorothalonil and its transformation have to be described. The following equation for first-order reaction kinetics was used:

$$dA_h/dt = k_{ch} A_c - k_h A_h$$

with: $A_h$ = amount of HTI, μmole;
$t$ = time, days;

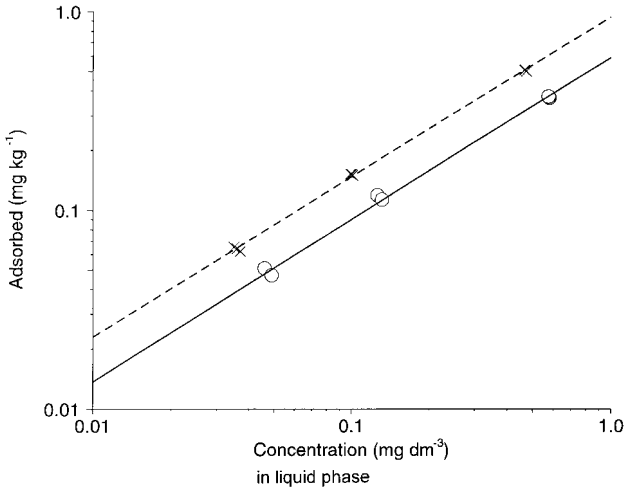


**Figure 1.** Adsorption of metamitron to topsoil materials from (○) Wassenaar M and (×) St Maartensbrug fields. Lines: calculated Freundlich adsorption isotherms.

$k_{ch}$ = rate coefficient for transformation of chlorothalonil to HTI, $day^{-1}$;
$A_c$ = amount of chlorothalonil, μmole;
$k_h$ = rate coefficient for transformation of HTI, $day^{-1}$.

The solution of this equation obtained by integration is:

$$A_h = \left(\frac{k_{ch}A_{c0}}{k_h - k_c}\right)[\exp(-k_c t) - \exp(-k_h t)]$$

with: $A_{c0}$ = initial amount of chlorothalonil, μmole;
$k_c$ = rate coefficient for transformation of chlorothalonil, $day^{-1}$.

The values of the rate coefficients $k_c$, $k_{ch}$ and $k_h$ were obtained by non-linear regression analysis, using the Genstat 5 statistical package.[7]

It is desirable to compare the transformation rates in soil examined in the present study with published rates for the same pesticides. However, different authors have used different incubation temperatures, which greatly affects the transformation rate. For the sake of comparison, the measured rates of transformation were translated to 20 °C, using a simplified form of the Arrhenius equation.[8]

$$k_{t,T} = k_{t,Tr} \cdot \exp[\gamma(T - Tr)]$$

with: $k_{t,T}$ = transformation rate coefficient ($day^{-1}$) at temperature $T$, K;

$k_{t,Tr}$ = transformation rate coefficient ($day^{-1}$) at reference temperature $Tr$, K;
$\gamma$ = empirical parameter, $K^{-1}$.

The average value of $\gamma = 0.08\,K^{-1}$ for many published results[8] was used for the translation to the reference temperature in the present comparisons.

## 3 RESULTS

### 3.1 Adsorption

#### *3.1.1 Metamitron*

The measured values for the adsorption of metamitron to the top layer materials from the Wassenaar M and St Maartensbrug fields are given in Fig 1. The Freundlich isotherm gives a good description of the adsorption at the three concentration levels in solution. The adsorption of metamitron to the St Maartensbrug soil was stronger than to the Wassenaar M soil. This corresponds with the higher organic matter content of the former soil (Table 1). The slopes of the isotherms were almost the same.

The Freundlich adsorption coefficient for the Wassenaar M soil was calculated to be $K_f = 0.60\,dm^3\,kg^{-1}$, while the Freundlich exponent was $n = 0.82$. The corresponding values for the St Maartensbrug soil were: $K_f = 0.94\,dm^3\,kg^{-1}$ and $n = 0.81$. Calculation of the adsorption coefficient $K_{om}$ on the basis of soil organic matter yielded values of $60\,dm^3\,kg^{-1}$ (Wassenaar M) and $55\,dm^3\,kg^{-1}$ (St Maartensbrug).

#### *3.1.2 HTI*

The results of the measurements of the adsorption of HTI to the topsoil materials from the Wassenaar C and St Maartensbrug fields are given in Fig 2. The adsorption at the three concentration levels could be described with the Freundlich adsorption isotherm. At the two upper concentration levels, the adsorption of HTI to the St Maartensbrug soil was somewhat stronger than to the Wassenaar C soil. The slope of the plot was somewhat steeper for the St Maartensbrug soil.

The Freundlich coefficient for the adsorption of HTI to the Wassenaar C soil was calculated to be $K_f = 3.11\,dm^3\,kg^{-1}$, while the Freundlich exponent was $n = 0.92$. The values calculated for the St Maartens-

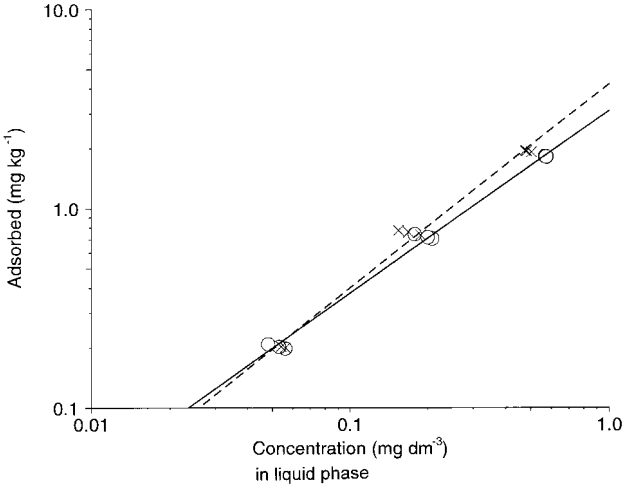


**Figure 2.** Adsorption of HTI to topsoil materials from (○) Wassenaar C and (×) St Maartensbrug fields. Lines: calculated Freundlich adsorption isotherms.

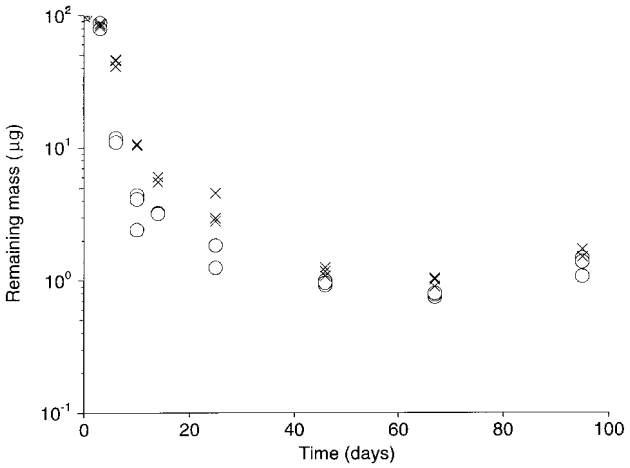


**Figure 3.** Quantities of metamitron at various moments during incubation (at 15 °C) in topsoil materials from (○) Wassenaar M and (×) St Maartensbrug fields.

brug soil were $K_f = 4.25\,dm^3\,kg^{-1}$ and $n = 1.03$ (almost linear isotherm). The values of the adsorption coefficient $K_{om}$ of HTI on the basis of soil organic matter were calculated to be $270\,dm^3\,kg^{-1}$ (Wassenaar C) and $250\,dm^3\,kg^{-1}$ (St Maartensbrug).

## 3.2 Transformation

### *3.2.1 Metamitron*

The results of the incubation of metamitron in the Wassenaar M topsoil at 15 °C are given in Fig 3. After the first three days, about 84% of the dose remained. This was followed by a period with comparatively rapid transformation to about 3% of the dose after 14 days. In the last period, transformation of the small remaining fraction was slow.

The quantities of metamitron measured after various incubation times in the topsoil materials from St Maartensbrug are also shown in Fig 3. After three days, an average of 85% of the dose remained. After that, the transformation was comparatively rapid until about 6% of the dose was left after 14 days. The transformation of the last fraction of metamitron, of the order of a few percent, was slow.

The transformation of metamitron in the Wassenaar soil during the first 14-day period was described by first-order kinetics. The first-order rate coefficient was calculated to be 0.28 $day^{-1}$, which corresponds to a half-life of 2.5 days. When the transformation of metamitron in the St Maartensbrug soil during the first 14 days was described by first-order kinetics, a first-order rate coeffcient of 0.23 $day^{-1}$ was calculated. This corresponds to a half-life of 3.0 days.

The rate of transformation of metamitron in these soils was unexpectedly high. Presumably, the micro-organisms in the two soils have adapted themselves to metamitron, because of its regular application to the flower-bulb crops. The slow transformation of the last fraction of metamitron in the soils may have resulted from the decline in availability for microbial attack.

### *3.2.2 Chlorothalonil and HTI*

The transformation of the amount of chlorothalonil incubated (at 15 °C) in the topsoil material from the Wassenaar C field is shown in Fig 4. At 10 days after the start, an average of 60% of the dose was left; after 35 days this was 12%. The transformation of chlorothalonil over the first two months could be approximated by first-order kinetics, with a rate coefficient $k_t$ of 0.063 $day^{-1}$. This corresponds to a half-life of 11 days. Low levels of chlorothalonil were still measurable after a long time: 0.3% of the dose after 126 days and 0.2% of the dose after 258 days.

Figure 4 also shows the formation of HTI from chlorothalonil in the Wassenaar C topsoil. The maximum amount of HTI corresponded to 40% of the dose of chlorothalonil and was reached at 84 days after the start. Over the subsequent six months, the decline of HTI from this maximum was very slow.

The transformation of the amount of chlorothalonil incubated in the topsoil material from St Maartensbrug is shown in Fig 5. At 10 days after the start, an average of 53% of the dose of chlorothalonil was left; after 35 days this was 14%. For the first two months, the transformation of chlorothalonil can be described by first-order kinetics. The rate coefficient $k_t = 0.053$ $day^{-1}$ corresponds to a half-life of 13 days. A low level of chlorothalonil could be measured for a long time: 0.7% of the dose after 126 days and 0.3% of the dose after 258 days.

At first, HTI gradually increased during the transformation of chlorothalonil in the St Maartensbrug soil (Fig 5). The maximum amount of HTI was reached after 84 days of incubation and corresponded to 40% of the initial amount of chlorothalonil. After this, HTI declined very gradually; after 258 days of

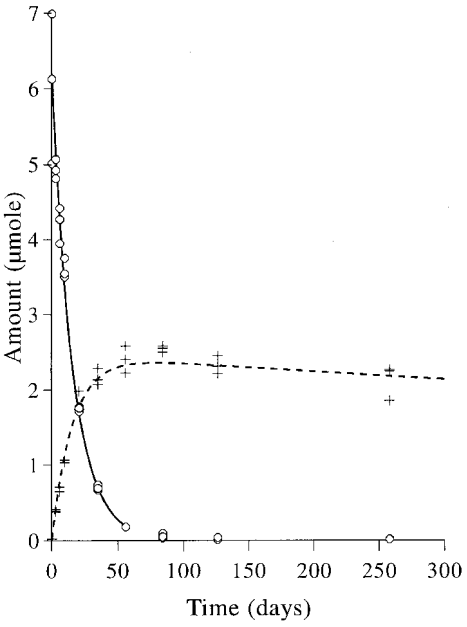


**Figure 4.** Transformation of (○) chlorothalonil and (+) HTI over time during incubation in the Wassenaar C soil at 15 °C. Lines: calculated with first-order kinetics.

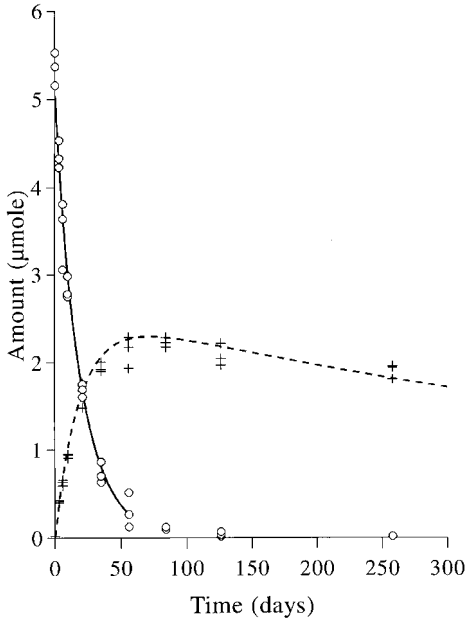


**Figure 5.** Transformation of (○) chlorothalonil and (+) HTI over time during incubation in the St Maartensbrug soil at 15 °C. Lines: calculated with first-order kinetics.

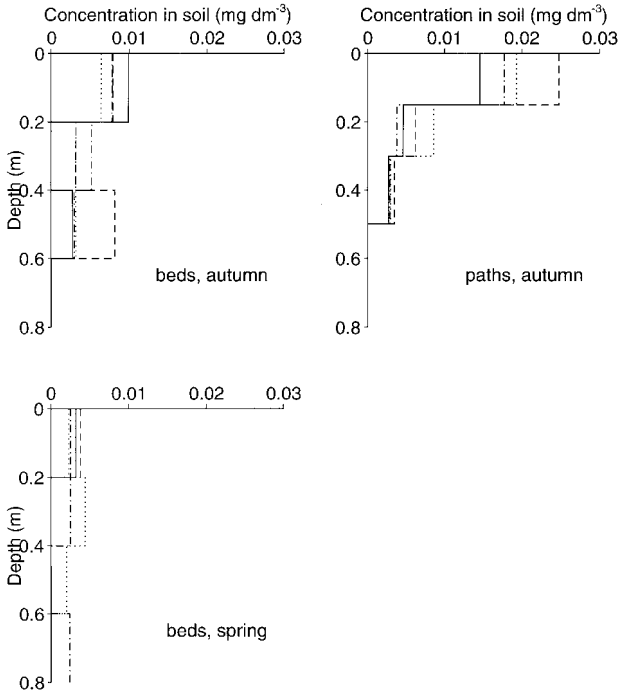


**Figure 6.** Concentrations of metamitron in the soil profiles of the beds and paths in the Wassenaar M field in the autumn of 1993 and the spring of 1994.

incubation, the amount of HTI still corresponded to 36% of the dose of chlorothalonil.

Both the transformation of chlorothalonil and the formation of HTI could be described by first-order kinetics (Figs 4 and 5). It was calculated that in the Wassenaar C soil 40% of the dose of chlorothalonil was transformed into HTI, while in the St Maartensbrug soil this was 49% of the dose. It is difficult to calculate the rate of transformation of HTI in these two soils, because of the combination of its slow transformation and the spread in the measured values. The extrapolated half-life of HTI in this study could be a few years. The microbial activity in the incubated soil batches may have decreased with time.

### 3.3 Concentrations in the field

*3.3.1 Metamitron*

In the early spring of 1993, before metamitron was applied in the growing season of that year, the Wassenaar M soil profile (down to 0.8 m) contained 0.010 kg ha$^{-1}$ of metamitron, while the St Maartensbrug soil contained 0.005 kg ha$^{-1}$ of metamitron.

In the top layer of the soil (0.05 m) sampled one day after the application of metamitron in Wassenaar (on 21 April 1993), 46% of the dosage of metamitron was measured. In the St Maartensbrug field, 50% of the dosage was measured in the top layer samples (0.05 m) taken one day after the application (on 20 April 1993). A small fraction of the dosage may have been lost during application, due to spray drift. The lily plants were very small at this stage, so there was hardly any interception by the crop. In view of the rapid transformation of metamitron in the soils, the difference can be partly explained by transformation during the first day in the field and during sample handling at the laboratory. However, additional processes may have contributed to the difference between the measured and expected amounts of metamitron in the top layer.

The top 0.05 m of the St Maartensbrug field was sampled on 30 June 1993, 42 days after the last metamitron spraying (on 19 May 1993). At that time, only 1.4% of the last dosage of 2.1 kg ha$^{-1}$ was left in this layer.

The concentrations of metamitron measured in the soil profile of the Wassenaar M field are presented in Fig 6. After the growing season (on 8 November 1993), the average concentration in the top layer was highest. There was a gradual decrease of the concentration with depth to below the determination limit of 0.002 mg dm$^{-3}$. The average concentration in the top layer in the paths was higher than that in the beds. In the next spring (30 March 1994), the concentrations of metamitron in the soil of the beds (Fig 6) had decreased to very low levels throughout the profile.

In the autumn of 1993, the total amount of metamitron in the soil profile of the beds corresponded to 0.03 kg ha$^{-1}$, that in the profile of the paths to 0.05 kg ha$^{-1}$. This is only a small fraction of the cumulative dosage of 5.3 kg ha$^{-1}$ of metamitron applied in the period from 21 April to 8 September (Table 2). In the growing season, the soil cover by the lily crop on this field was 40% at most, so much of the dosage was deposited on the soil surface. The amount of metamitron measured in the soil profile of the beds in the spring of 1994 corresponded to 0.01 kg ha$^{-1}$.

Figure 7 shows the concentrations of metamitron measured in the soil profile of the St Maartensbrug field. The average concentration was highest in the top

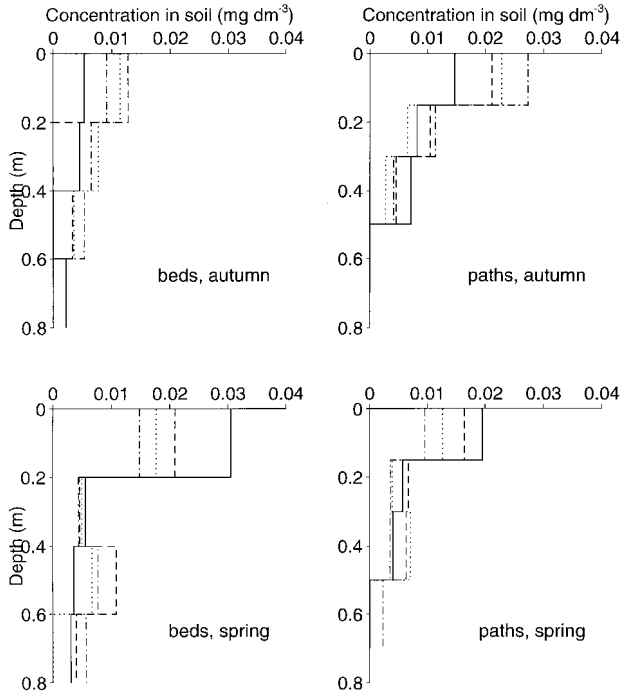


**Figure 7.** Concentrations of metamitron in the soil profiles of the beds and paths in the St Maartensbrug field in the autumn of 1993 and the spring of 1994.

layer and decreased gradually with depth to low levels below 0.6 m. In the autumn after the growing season (on 25 October 1993), the average concentration in the top layer of the beds was lower than that in the paths. This difference was similar to that in the Wassenaar field. Remarkably, the average concentration in the top layer of the beds in the next spring (6 April 1994) was higher than that in the autumn. In the soil profile of the paths, there was a limited decrease in the concentration during the winter season. The effect of the ploughing of the field on 4 November 1993 on the distribution of metamitron in the soil is not clear. Heterogenous distribution of the metamitron residue in the soil may have led to substantial sampling variation.

The total amount of metamitron in the soil profile of the St Maartensbrug field in the autumn after the growing season corresponded to 0.04 kg ha$^{-1}$ (beds) and 0.06 kg ha$^{-1}$ (paths). This is only a very small fraction of the cumulative dosage of 6.3 kg ha$^{-1}$ of metamitron applied during the growing season (Table 2). As the soil cover by the crop was 40% at most, much of the dosage was deposited on the soil surface. The amounts measured in the soil profiles in the next spring corresponded to 0.07 kg ha$^{-1}$ (beds) and 0.04 kg ha$^{-1}$ (paths).

In the water samples taken from the six ground-water tubes in the Wassenaar M field, residues of metamitron were found at two times: in October 1993 and in January 1994. The average concentration was 0.13 µg dm$^{-3}$ ($n = 12$; $s = 0.03$ µg dm$^{-3}$). At the other four sampling times (April, July and September 1993; March 1994), metamitron was below the detectable level (0.07 µg dm$^{-3}$). At the St Maartensbrug field, metamitron was found in a fraction of the ground-water samples taken in October 1993 and January 1994. The average concentration at these sampling moments was 0.09 µg dm$^{-3}$ ($n = 12$; $s = 0.06$ µg dm$^{-3}$). The concentration of metamitron in the samples taken at the other four moments was below the detectable level. The analyses of metamitron in the upper ground-water were not checked with a second analytical method, so the actual concentrations may have been lower than those given here.

### *3.3.2 Chlorothalonil and HTI*

The soil profile of the Wassenaar C field was sampled on 29 March 1993, with a view to analysing the soil for residues of HTI from applications of chlorothalonil in previous years. The amount of HTI in the soil profile corresponded to 0.02 kg ha$^{-1}$. A cumulative dosage of 3.1 kg ha$^{-1}$ of chlorothalonil had been applied to the tulip crop grown on the field in 1992. The residue of HTI in the soil profile of the St Maartensbrug field, before the 1993 application of chlorothalonil, was found to be at the same very low level. Chlorothalonil had been applied to this field in the spring of 1992, in two dosages of 0.75 kg ha$^{-1}$.

One day after the application of chlorothalonil to the Wassenaar C field on 8 April 1993, the top 0.05 m layer of the soil in the beds was sampled for analysis. The amount of chlorothalonil corresponded to 0.18 kg ha$^{-1}$, ie only 24% of the calculated dosage of 0.75 kg ha$^{-1}$. Some loss may have occurred by spray-drift during application. Deposition of chlorothalonil on the crop (which covered about 20% of the soil) can explain only part of the low areic mass in and on the top layer after one day. Since transformation of chlorothalonil in the soil can only have made a small contribution to the decline in one day, it would appear that other processes played a role in the decline of chlorothalonil in and on the top layer during the first day.

On 19 May 1993, the top layer of the beds in the Wassenaar C field was sampled again for chlorothalonil analysis. The last dosage of 0.75 kg ha$^{-1}$ had been applied on 1 May 1993. The quantity of chlorothalonil in the top layer after 18 days corresponded to 4% of

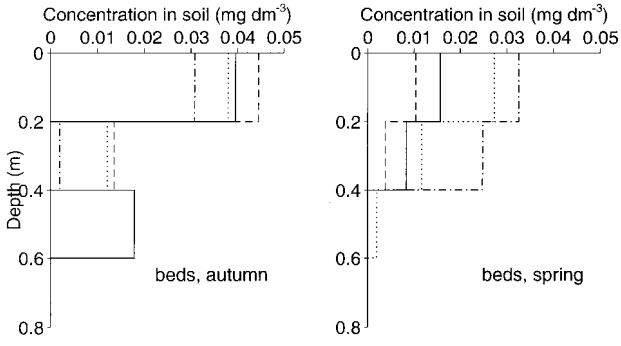


**Figure 8.** Concentrations of HTI in the soil profiles of the beds of the Wassenaar C field in the autumn of 1993 and the spring of 1994.

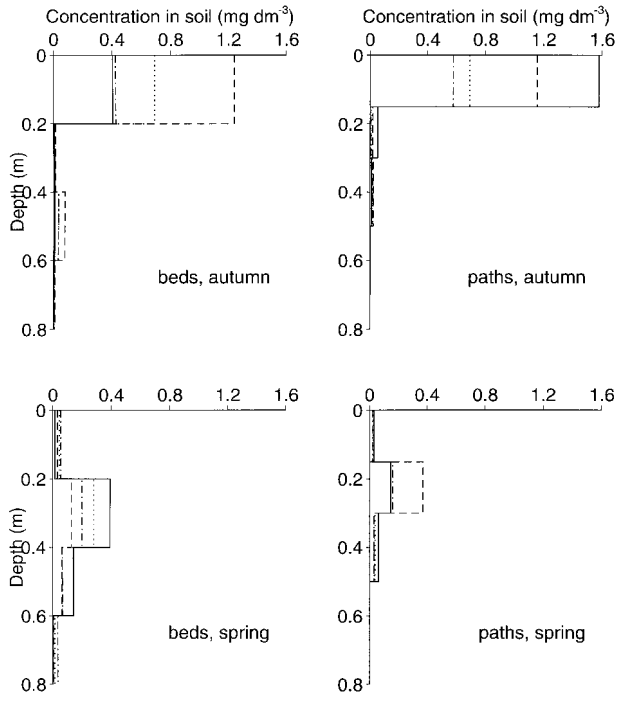


**Figure 9.** Concentrations of HTI in the soil profiles of the beds and paths of the St Maartensbrug field in the autumn of 1993 and the spring of 1994.

the dosage. Much of the dosage had been intercepted by the crop (which covered about 75% of the soil). Transformation of chlorothalonil in the soil may have reduced its initial mass in soil by about 70%. Again, the areic mass of chlorothalonil in the top layer was lower than expected.

The top layer of the St Maartensbrug field was sampled on 30 June 1993, 10 days after the last application of 0.75 kg ha$^{-1}$ of chlorothalonil. The amount in the soil corresponded to 13% of the last dosage. Part of the dosage had been deposited on the crop (which covered about 40% of the soil) and transformation in the soil had reduced the initial amount by about 40%. Again, the amount of chlorothalonil in the top layer was lower than expected from the estimated contributions to the decline.

The concentrations of HTI measured in the soil profile of the beds in the Wassenaar C field in the autumn (8 November 1993), after the applications of chlorothalonil to the hyacinth crop, are shown in Fig 8. The highest concentrations were measured in the top 0.2 m of the soil. In the 0.2- to 0.4-m layer, very different concentrations were measured for the four field sections. In the 0.4- to 0.6-m layer, there was one comparatively high value, whereas HTI was below the detection limit of 0.002 mg dm$^{-3}$ in the other three sections. The soil had been rooted up (mainly in the top layer) at the harvest of the hyacinth bulbs and by the subsequent rotary harrowing, both in June 1993. The total amount of HTI in the soil profile corresponded to 0.10 kg ha$^{-1}$ (0.11 kg chlorothalonil equivalents per ha). This is only a small fraction of the cumulative dosage of chlorothalonil (2.25 kg ha$^{-1}$) in the growing season of the hyacinths (Table 2).

The concentrations of HTI measured in the Wassenaar C field in the next spring (30 March 1994) indicate that there had been some movement from the 0–0.2-m layer to the 0.2–0.4-m layer (Fig 8). Deeper in the soil (below 0.4 m), most concentrations were below the detection limit. The total amount of HTI in the beds in spring corresponded to 0.07 kg ha$^{-1}$ (0.07 kg chlorothalonil equivalents per ha). This indicates that there was only a gradual decrease in the amount of HTI in soil over the winter period.

The concentrations of HTI measured in the soil profile of the St Maartensbrug field in the autumn (25 October 1993) are shown in Fig 9. Both in the beds and in the paths, the compound was mainly located in the upper layer. The total amount of HTI in the soil profile of the beds corresponded to 1.47 kg ha$^{-1}$ (1.58 kg chlorothalonil equivalents per ha). The total quantity of HTI in the soil profile of the paths was similar: 1.57 kg ha$^{-1}$ (1.68 kg chlorothalonil equivalents per ha). This is only a fraction of the cumulative dosage of 9.0 kg ha$^{-1}$ of chlorothalonil applied to the field in the growing season of the lily crop (Table 2).

In the next spring (6 April 1994), HTI was mainly found in the second layer of the soil profile (Fig 9). Presumably, the ploughing of the soil (about 0.35 m deep) in the previous autumn (on 4 November 1993) had turned part of the soil in the top layer into the second layer. In addition, some downward movement of HTI may have occurred over the winter period. The total amount of HTI in the soil profile had decreased over the winter period; it corresponded to 0.81 kg ha$^{-1}$ (beds) and 0.42 kg ha$^{-1}$ (paths). The equivalent areic masses of chlorothalonil itself were 0.87 kg ha$^{-1}$ (beds) and 0.45 kg ha$^{-1}$ (paths).

The average concentration of HTI in the 30 ground-water samples taken from the six tubes in the Wassenaar C field on five occasions (period July 1993 to March 1994) was 0.2 μg dm$^{-3}$. In the 30 ground-water samples from the six tubes in the St Maartensbrug field, taken at five times during this period, the average concentration of HTI was 0.1 μg dm$^{-3}$. In four of the six ground-water samples which were also analysed by TNO Nutrition and Food Research using GLC, the presence of HTI at or above 0.1 μg dm$^{-3}$ was confirmed.

## 4 GENERAL DISCUSSION AND CONCLUSIONS

The values of the coefficient $K_{om}$ for the adsorption of metamitron to soil organic matter were calculated to be 60 dm$^3$kg$^{-1}$ (Wassenaar M) and 55 dm$^3$kg$^{-1}$ (St Maartensbrug). On the basis of earlier measurements on the adsorption of metamitron to soils,[1] the average value of $K_{om}$ was calculated to be 108 dm$^3$kg$^{-1}$ ($n = 18$; $s = 52$ dm$^3$kg$^{-1}$). Most of those soils had a substantial clay content (range 15 to 41%) and this soil component may have contributed to the adsorption of metamitron. It was found that, for soils low in organic matter, the clay fraction made a distinct contribution

to the adsorption of metamitron.[9] Direct use of adsorption data for loamy soils would thus lead to over-estimation of the adsorption of metamitron to soils low in clay content.

The values of the coefficient $K_{om}$ for the adsorption of HTI to soil organic matter were calculated to be 270 $dm^3kg^{-1}$ (Wassenaar C) and 250 $dm^3kg^{-1}$ (St Maartensbrug). This implies that the adsorption of HTI is moderate in such low-humic soils and that it may be rather strong in soils containing several percent of organic matter. These measurements remove part of the uncertainty in the Dutch pesticide regulation procedure on the mobility of HTI in soils. More information is needed on the contribution of other soil components, such as the clay fraction, to the adsorption of HTI in a wider range of soils.

Metamitron was transformed very rapidly in the two sandy soils used for growing flower bulbs. In the incubation studies, its half-life was only about three days and in the field only a small fraction of the cumulative dosage in the growing season remained in late autumn. This rapid transformation is remarkable, because an earlier study[1] had found that the average half-life for metamitron in 18 soils (at 20 °C) was 26 days. It seems that transformation in the flower-bulb soils was accelerated due to microbial adaptation, induced by the repeated application of metamitron over a period of several years. The effect of repeated application of metamitron on its rate of transformation in a sandy clay loam soil has been studied before.[10] It was found that the rate of transformation of metamitron in the laboratory increased as the number of previous treatments of the soil in the field increased. At 14 days after application of metamitron to field plots, its residue in previously treated plots was distinctly lower than in plots not treated before.[10] It was concluded that metamitron is vulnerable to accelerated microbial transformation in the soil when applied regularly at rather short intervals. The action of metamitron on the weeds via uptake from the adapted soils must thus be short-lived. However, the herbicide also acts via uptake by the weed leaves.

Some other recent papers have reported on the rate of transformation of metamitron in soil. When metamitron was incubated in moist loam soil at 20 °C, its half-life was found to be 15 days.[11] The rate of transformation of metamitron has also been measured (at 15 °C) in a loamy sand soil used for growing sugarbeet in a crop rotation scheme;[12] its half-life was 14 days (which corresponds to 10 days at 20 °C). When metamitron was incubated in moist sandy clay loam soil at 20 °C, its half-life was found to be 19 days.[13] It is interesting that the half-lives measured in the 1990s tend to be shorter than those measured in the 1980s (when the average was 26 days).[1] Unfortunately, the authors of the most recent studies do not give details of the history of metamitron application to their soils.

The last fraction of metamitron in the flower-bulb soils was only transformed at a low rate, as was apparent in both the incubation studies and the field experiments. Presumably, the availability of this residue to microbial transformation is low. Some of the herbicide may have diffused into the finest pores, which are hardly accessible to microbial activity.

One day after the spring application only about half of the dosage of metamitron was found in the top layer of the soils. Various processes may have contributed to the difference between the measured and calculated amounts. During spraying, spray-drift may take some of the herbicide out of the field. As the lily plants were still small, the interception by the plants was only a small fraction of the dosage. In view of the rapid transformation of metamitron in the soils, some transformation will have occurred during the first day and during the handling of the soil samples. On the basis of the low vapour pressure and other physicochemical properties of metamitron, its volatilisation from the soil is expected to be small.[14] Metamitron solution in water absorbs light (290 to 370 nm) in the sunlight spectrum, leading to photolysis,[15] so that some phototransformation of metamitron at the soil surface may occur. In a published field experiment,[16] the initial amount of metamitron in the topsoil was also distinctly lower than the calculated dosage.

Incubation of chlorothalonil in the two flower-bulb soils at 15 °C resulted in half-lives of 11 and 13 days, respectively. Translated to 20 °C, the half-lives can be expected to be 7 and 9 days. In a previous study,[4] chlorothalonil was incubated in three soils at 30 °C at the rather high initial content of 40 mg $kg^{-1}$. Translation of those results to 20 °C gives estimated half-lives of 7, 25 and 47 days, respectively. The results of an experiment incubating chlorothalonil in a moist silty loam soil[3] correspond to half-lives at 20 °C in the range of 5 to 12 days. So the half-lives of chlorothalonil measured in the present study are in the range of the lowest half-lives found in some published studies.

When chlorothalonil was measured in the top soil layer within a few weeks after application, its amount was lower than expected on the basis of the dosage minus the interception by the crop. Spray-drift can explain a small fraction of the loss from the field. In view of its physicochemical properties (low vapour pressure etc.), volatilisation of chlorothalonil from soil is expected to be low.[14] In a review on chlorothalonil,[17] the authors refer to an unpublished study showing only very slow phototransformation on soil surfaces. More information is needed on the processes that cause the net chlorothalonil load of the soil to be lower than expected.

The rate of transformation of HTI in the two soils of our incubation study was very low. No data on the rate of transformation of HTI in soil have been found in the literature. In the review on chlorothalonil,[17] reference was made to an unpublished incubation study with chlorothalonil, in which the transformation of HTI was also found to be slow.

The amounts of HTI measured in the soil profiles in

the autumn of 1993, after the chlorothalonil applications during the growing season, correspond to a comparatively small fraction of the dosage. In the Wassenaar C soil, 3.7% of the cumulative dosage of chlorothalonil remained as HTI; in the St Maartensbrug soil this was 16.3%. The last application of chlorothalonil in Wassenaar was on 21 May, so several months were available for the transformation of HTI. By contrast, the applications in St Maartensbrug continued until 20 September, which explains the comparatively high residue of HTI in this soil in the autumn. The extent of transformation of HTI in the soils in the winter period can be calculated from the difference between the amounts in the autumn of 1993 and the spring of 1994. In the Wassenaar C soil, 38% of the HTI was transformed during this period. For the St Maartensbrug soil, the transformation over the winter period was 40% of the amount of HTI present in the autumn.

Assessment of the rate of transformation of HTI in the soil during the growing season requires more frequent analysis of its concentration profile in the soil. A disadvantage of long incubation studies in the laboratory is that microbial activity may be expected to decrease due to the exhaustion of nutrients. In addition, the variation in soil conditions in the field may promote the transformation of HTI. Hence, research on the environmental factors which influence the rate of transformation of HTI in soils is also needed.

The movement of the slowly transformed HTI through the soil profiles to the ground-water was reduced by its moderate adsorption to the soils. Presumably, the ploughing of the soil in the autumn contributed substantially to the presence of the highest concentration of HTI in the layer below the top layer. Low concentrations of HTI were measured in the upper ground-water level below these flower-bulb soils, which are vulnerable to pesticide leaching. Studying the extent of leaching of HTI in other agricultural soils under field conditions is desirable.

## ACKNOWLEDGEMENTS

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